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A STUDY OF SOME NEW

SEMIPERMEABLE MEMBRANES.

DISSERTATION

Submitted to the Board of University Studies of the Johns Hopkins University in Conformity with the Requirements for the Degree of Doctor of Philosophy.

-by-

J. P. Coony, S.J.

1903.

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ACKNOWLEDGMENT.

To Professor Morse, without whose initiative, kindly assistance and experienced direction this work could not have been carried out, the author wishes to make grateful acknowledgment. No less is he indebted to President Remsen, whose lectures have been both guidance and inspiration. The able instruction of Professor Jones, Dr. Shattuck and Professor Clark, likewise calls for appreciative recognition.

A STUDY OF SOME NEW SEMIPERMEABLE MEMBRANES.

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It is quite unnecessary, in giving an account of work done on the subject which forms the title of this paper, to review even briefly, the work and measurements of Pfeffer,[1] the brilliant theoretical work of van't Hoff[2] founded on them, or the extremely valuable results achieved by De Vries,[3] Tammann,[4] and Hamburger,[5] men who were stimulated to undertake their great work by van 't Hoff's conclusions. The great importance of this question of osmotic activity has made the scientific world familiar with these results. And if subsequent progress has failed to correspond to these brilliant beginnings, the explanation is to be sought for in the almost insurmountable difficulties everywhere to be met with.

The failure of so many attempts to repeat Pfeffer's work demonstrated the fact that only by great good fortune

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(1) Osmotische Untersuchung, (1877).
(2) Zeitsch . Phys. Chem. 1, 481 (1887).
(3) ibid. 2, 415 (1888).
(4) Wied. Ann. 34, 299 (1888).
(5) Zeitsch . Phys. Chem. 6, 319 (1890).

could an experimenter hope to secure a good membrane and a reliable cell by the methods employed by this investigator. Indeed, no work comparable to his had been done until a new method,[1] devised by Morse and Horn and further perfected by Morse[2] and Frazer, gave well founded hopes of easily and surely forming quite perfect membranes. Most interesting indeed are the results of these last workers, showing the rapidity with which a satisfactory membrane develops a pressure sufficient to burst the highly resisting materials which they employed. Near the end of the paper last mentioned we read the brief history of a cell in which the measurement of the osmotic pressure of a normal solution of sugar was attempted. "Resistance of the membrane not exactly known, but over 200,000 ohms. The solution of sugar fresh and free from invert sugar. Cell set up at 5 P.M. Pressure at 5.10 P.M., 7.89 atmospheres; at 6.45 P.M., 31.41 atmospheres (corrected). Temperature 24 .9. Shortly after the second reading the glass tube was shattered."

The very satisfactory results recorded in this last paper gave a new impetus to work in this field and the pros-

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(1) Amer. Chem. Jour. 26, 80 (1901).
(2) Ibid. 28, 1 (1902).

pect of soon being able to measure directly and with accuracy the osmotic pressure of normal solutions, and probably of yet higher concentrations, made clear the immediate desirability of a number of semipermeable membranes of a sufficiently wide range of chemical characteristics to permit of the selection, in each individual case, of some one membrane which should be chemically inert with regard to the particular substance the osmotic pressure measurements of which were desired. For the discovery of such membranes the electrolytic method seemed to promise speedy and sure results, and it was accordingly made use of in the following investigation.

In testing the various semipermeable membranes investigated in this laboratory, two kinds of cups have been employed, the smaller kind has a capacity of about 15 c.c. and seems in general to possess a finer texture and to have been burned to a greater degree of hardness than the larger variety, the capacity of which varies from 170 to 200 c.c. This larger cell, because of its shape, is commonly called the bottle cell.

THE PRELIMINARY PREPARATION OF THE CELL.

This preliminary treatment consists first in melting shellac within the neck of the cell until a firm coating is secured, covering all that portion of the cell wall which could be affected by the introduction and removal of the rubber stoppers employed. The purpose of this film of shellac is to make sure that no portion of the semipermeable membrane formed will be exposed to the danger of rupture by friction or by the strains set up in the neck of the cell by the tightly fitting stoppers. By this means is precluded all possibility of a leakage of the solutions through portions of the porous wall where either no membrane has been formed, or, if formed, ruptured or locally removed in the process of closing the cell.

The next step is to free the cell wall of all soluble materials, especially of the air contained within the pores. As the simple apparatus here employed is used also in the formation of the membrane, it will be well to describe it in detail. A rubber stopper through which passes the direct arm of a glass T tube of say 10 mm. internal diameter is fitted into the neck of the cell. This admits a second glass tube of three or four mm. diameter. This sec-

ond tube, the purpose of which is the transmission of liquids into the cell, reaches quite to the bottom of the cell and is the outlet from a reservoir of suitable capacity. The flow from this into the cell can be regulated at will by a pinch cock on the rubber connection. Surrounding the lower end of this second tube is the inner platinum electrode, the platinum connection of which passes also through the T tube. The horizontal arm of the latter serves as an escape for the liquids introduced into the cell from the reservoir. By this means the liquid within the cell can be renewed as desired without any interruption to the process, And in most cases continual change is advisable. The cell is then placed in a beaker, of a depth at least equal to its own height, and is surrounded by the outer electrode. In the process of washing cells, and frequently also in building up the membrane, this electrode is of platinum, though in the latter process, other workers in this laboratory have found electrodes of Cu, Ni, Sn, Zn, etc., to be more satisfactory when the membrane to be deposited was a salt of one of these metals. When the membrane is some insoluble ferric salt, both electrodes must be of platinum, as a test made with an iron anode showed that by the electrolytic action an appreciable portion of ferrous compound

was formed together with the ferric salt.

The cell walls should first be thoroughly wetted from either the outside or the inside; this is done in order to avoid the probable entrapping of air between the advancing walls of liquid should the latter be applied to both sides of the cell wall at about the same time. When thus wetted, both the cell and the beaker in which it stands are filled with a 0.05% solution of potassium sulphate in recently boiled distilled water. With such apparatus the process of washing is easily carried out. The inner electrode is made the cathode and the current intensity so regulated that the endomose amounts to 8 or 10 c.c. per minute. The outer solution needs replenishing at times to supply loss and to keep the cell covered, and both outer and inner solutions require occasional renewal, as they shortly become weak in cations and anions respectively. Two hours of this treatment is followed by a similar treatment with boiled distilled water. The current is passed until a very low conductivity shows the nearly complete absence of potassium sulphate. This leaves the cell walls quite free of foreign materials, and the membrane may now be introduced, or the cell may be kept in distilled water until the operator is ready to proceed to this step.

THE FORMATION OF THE SEMIPERMEABLE MEMBRANE.

The Electrical Equipment - The current employed is usually taken from the storage batteries whose combinations permit the use of any potential between 2 and 110 volts. Connections are easily established, also, with 2 dynamo circuits of 110 and 220 volts respectively; while 3 rotary transformers furnish currents at any desired potential below 300 volts. In the larger and coarser cells low voltages are always found necessary in the earlier stages of the process; frequently 12, and at times even 6 volts marking the upper limit of the current which may safely be employed. In such cases, the use of a stronger current seems to effectively prevent any rise in the electrical resistance of the membrane. It is thought that under such conditions the membrane is unable to bridge over many of the pores in the cell wall, which, by a less vigorous treatment might be effectually stopped. Thus a large and unvarying cross-section of the liquid is left for the unimpeded passage of the ions. The safer, and indeed, more expeditious method seems to be to confine the current to limits of one, or at most two-tenths of an ampere, raising the voltage

somewhat as the resistance of the membrane rises; though an exception seems to be necessary in the case of the Prussian Blue membrane. With this membrane no good results were obtained until either a small current for a long period, or a large current for a shorter time had almost choked the cell walls with the amount of the precipitate formed.

The Solutions - The sulphates or nitrates of the metals were preferably employed. It is evident that when platinum anodes are used the chlorides are necessarily barred.

Concentrations - Though varying conditions have made changes in concentration advisable, the practice of Morse and Horn and of Morse and Frazer of generally using N/10 solutions has been found to give the best results. Theoretically, this question of concentrations should be determined by a consideration of the relative dissociations of the electrolytes at the concentrations employed, as also of the relative ionic velocities of the two constituents of the membrane. But the practical solution is much more easily carried out, and consists in simply observing the position of the membrane- whether within, or upon either edge of the porous wall- and in changing the relative concentrations accordingly.

While no systematic study has been made of the advantages or disadvantages of the various positions in which the membrane may be deposited, it is obvious that a membrane formed on the outer edge of the wall can have no support whatever against pressures from within. The fact is, that cells in which the membrane has been deposited upon the inner edge of the wall have been found to be uniformly much more active than those in which the membrane was formed within the wall. This was to be expected, as diffusion takes place comparatively slowly within a porous body of close texture and considerable density; and instead of having the semipermeable membrane as a fine partition sharply separating pure water from a solution of say normal concentration, the incoming water would soon so dilute the solution in the pores of the wall that the concentration at the membrane would probably fall far below one-tenth normal, and the activity, as indicated by the rate of flow of the water through the membrane, would be correspondingly low. If, on the contrary, the semipermeable membrane is on the inner edge of the wall, the practically undiminished concentration of the solution within and the pure water circulating through the porous wall are separated only by the thin membrane, and the maximum flow will be observed.

In the question of measuring osmotic pressures also- and for the same reason - a maximum pressure could hardly be expected, even after a very long time, if the membrane is within the wall. In consequence, efforts have been made to so correlate the concentrations of the two electrolytes that the semipermeable membrane should form upon the inner edge of the wall; and as experiment has shown that by using high relative concentrations within, the precipitate can be formed even in the outer electrolyte, and vice versa, the matter of position is under complete control. In practice, a beginning is made with concentrations probably correct, regard having been had for ionic velocities and dissociations of the electrolytes, and, if the membrane forms, where it is desired, as is commonly the case, no change is made. Otherwise, one or the other solution is diluted accordingly.

TO FORM THE SEMIPERMEABLE MEMBRANE.

When the cell has been prepared and the apparatus set up as before described, connection is made with the proper electrical terminals, and the electrolytes are introduced nearly simultaneously. The electrical resistance

falls during the short period required for the electrolytes to displace the water from the pores of the wall and rises as soon as the formation of the membrane begins. Under proper conditions, the resistance continues to increase until a maximum has been reached which corresponds to the character of the porous wall and the capabilities of the particular membrane. These observations coincide with conclusions reached by Morse and Horn, who, working with cups of considerable porosity, found that the resistance of the membrane could not be raised above a certain point. This maximum seems to be determined by the number and size of those pores which the membrane is unable to bridge.

If, after a delay of some days, the membrane-forming process is repeated, a considerably higher maximum resistance is usually obtained. This second maximum is seldom exceeded in later repetitions, even though these be quite numerous. If, however, the concentrations be so changed as to form the membrane in some new position, the resistance becomes quite irregular. Such irregularity was very marked in the earlier work. Instances also occurred of the resistance falling considerably below the maximum by the mere continuance of the process. This phenomenon is thus far without a satisfactory explanation.

TESTING THE MEMBRANE.

After the membrane has been formed the cell is washed thoroughly with distilled water, filled with the desired solution - usually a sugar solution exactly normal - closed with a tightly fitting rubber stopper containing either a manometer or a simple delivery tube. It is then placed in a vessel containing sufficient distilled water to rise above the highest level reached by the membrane. The membrane may be tested for activity, that is, for the rate of flow of the pure solvent through the membrane into the solution within; or, it may be tested for the pressure developed with a given concentration. In the former case the delivery tube is so arranged that its lowest point is 5 - 10 mm. above the level of the outer liquid. The cell is, in consequence, always operating against this slight pressure. If it is desirable to test the membrane for pressure - and this was done only in the early part of the work - the rubber stopper contains a closed manometer in which the compression of a volume of carefully purified air indicates the pressure then obtaining.

THE VARIOUS MEMBRANES.

THE FERRIC HYDROXIDE MEMBRANE - The properties of this well known precipitate, ferric hydroxide, seem such as to make it suitable in the highest degree for a semipermeable membrane. Its insolubility, its firm gelatinous consistency, are almost too well known to all those who have attempted the gravimetric determination of iron. The difficulty experienced in washing the precipitated hydroxide at once suggests the idea of impermeability with regard to dissolved materials. Its chemical inertness with regard to most basic substances strongly recommend it for the measurement of the osmotic pressure of this class of compounds, and it was accordingly the first membrane to be studied.

As the only ferric salt immediately obtainable was the chloride which is manifestly unsuitable for use with platinum electrodes, the first attempt was made with ferrous sulphate, giving a membrane of ferrous hydroxide. The expansion of this upon oxidation to the ferric hydroxide would, it was thought, produce an extremely close semipermeable membrane. A bottle cell of 185 c.c. capacity was filled with a 1/15 normal solution of ferrous sulphate, to which was added a considerable amount of carefully washed

ferric hydroxide precipitate, introduced for the purpose of taking up the sulphuric acid set free by the electrolysis. Outside, a 1/30 normal solution of sodium hydroxide was employed. This lower concentration was thought sufficient because of the much higher velocity of the hydroxyl ions. The membrane began forming almost immediately, and with a potential of 33 volts the resistance of the cell increased quite regularly at the rate of nearly 20 ohms per minute, reaching 825 ohms in forty-five minutes. The rise in resistance was less rapid after this, and over an hour was required to reach the maximum of 1000 ohms. The resistance an hour later marked 800 ohms.

The cell was next thoroughly washed with distilled water, then immersed in the same liquid, while through the interior air bubbles were continuously forced during eighteen hours. How complete was the oxidation was never known. The membrane, however, never exhibited any osmotic activity and attention was next turned towards the preparation of pure ferric salts; the sulphate, the nitrate and the acetate. When these were obtained cell II. of the same kind was filled with a 1/2 normal ferric sulphate solution, while the outer liquid was a 1/12 normal sodium hydroxide

solution. Here the resistance when the membrane first began to form was 12 ohms. In 45 minutes it rose to 385 ohms. The cell was then allowed to stand over night in distilled water, the formation of the membrane being resumed on the following morning. The resistance now rose rapidly, going beyond 1000 ohms within thirty-five minutes. At this point the cell was washed, and then set up with a normal sugar solution, but without manifesting any activity. The formation of a successful membrane in this cell was next attempted from ferric nitrate. The resistance of the membrane reached a maximum of 2680 ohms one hour after starting, and in the next fifteen minutes dropped to 2300 ohms. Here again the cell was washed, and again set up with the normal sugar solution, but without a more favorable result than before. In the third attempt, the concentration of the sodium hydroxide solution was made equal to that of the ferric nitrate within. This gave a low resistance varying not far from 100 ohms, and the fast moving hydroxyl ions passing entirely through the wall formed an abundant precipitate of loose ferric hydroxide inside the cell. A last attempt was made employing ferric acetate. The highest resistance obtained was 175 ohms. The cell showed no osmotic

activity with either a normal sugar solution or a twice normal solution of sodium chloride. One week later the outer liquid was intensely salt; from which we infer that the ferric hydroxid membrane, in such a wall is completely permeable with regard to this substance.

CELL No. XVIII. - This cell, of the same grade, was tried six weeks later when considerable experience had been gained with other membranes in this same type of cell. Three days were spent in futile efforts to form an active membrane of ferric hydroxide. The cell when set up with a normal sugar solution showed no activity, and twenty-four hours later the marked sweetness of the outer solution proved either that this kind of cell does not properly support a ferric hydroxide membrane, or that this membrane is permeable as well towards sugar as towards sodium chloride.

With the small cells of finer texture the ultimate result was widely different. In two hours with a 1/10 normal solution of ferric acetate within and a 1/20 normal solution of sodium hydroxide without, the resistance rose to 9000 ohms - the maximum resistance developed in this cell. This was, comparatively speaking, a lower figure than those obtained on the larger cells; regard being had for the cor-

responding ly large cross-section of conductive membrane. Yet, when set up with a 1/2 normal sugar solution, the liquid rose rapidly to the top of the open manometer tube. This had a length of 1.2 meters and a bore of about 1 millimeter. The rate of rise of the liquid was about 10 mm. per minute. This cell continued to flow freely during the next three days. It was then taken down and fitted for measuring higher pressures. The membrane was reinforced by a further electrolytic deposition of ferric hydroxide and the cell after having been filled with a normal sugar solution was fitted with a closed manometer and placed in the distilled water. The highest pressure recorded was 0.5 atmospheres. This seemed to indicate that the insufficiently supported membrane gave way locally, allowing the leakage at this pressure to equal the inflow of water. The known activity of the membrane and the amount of sugar passing into the outer water could not otherwise be accounted for.

A second cell of this type, which had failed to produce an active membrane by a similar treatment with ferric phosphate, was tried with the ferric hydroxide membrane. This cell when a resistance of 3000 ohms had been reached, was set up with an open manometer tube 2.4 meters in height.

The level of liquid in this tube rose at the very rapid rate of 92 millimeters per minute when at the height of 600 millimeters, and the sugar solution flowed freely from the top of the tube during the two days it was allowed thus to remain. Four other cells of the same type were tried with this membrane, the results being uniformly satisfactory as regards activity, but never showing a pressure much in excess of 1 atmosphere. Of these cells the flow of one was measured. The capacity of the cell was 16 c.c. and it was delivering at a pressure of about 35 mm. water. The figures record the total delivery after twenty-four periods.

First 24 hours	8.0c.c.
Second "	13.2 "
Third "	16.2 "
Fourth "	18.4 "

These cells were afterwards broken and their membranes carefully examined. They appeared firmer and more uniform than the other membranes tested in this investigation. There is every probability that in a porous wall of a sufficiently fine and uniform texture this membrane will prove to be of great value. The cells thus far tried with this membrane are known to give unreliable support under

pressure: indeed, the cells of the coarser type failed, even when no pressure was developed; and hence we may reasonably ascribe to them the deficiencies manifested.

THE FERRIC PHOSPHATE MEMBRANE - A fair trial of this membrane cannot, it is probable, be made until a cell wall of the desired texture is forthcoming. Two cells of the finer grade were given careful trials, yet they failed to indicate any osmotic action whatever. These trials were not sufficiently exhaustive to prove the incapability of these cells to support the membrane, yet it is clear that the membrane could not be satisfactory in them. The appearance of the ferric phosphate precipitate is most promising, and its chemical character such as to make it extremely valuable if an active membrane can be developed.

THE MANGANESE FERROCYANIDE MEMBRANE - This precipitate is of fine grain with very little tendency toward agglutination, and it does not offer the appearance of a promising semipermeable membrane. The color, white at first, changes on standing to a delicate pale green. This change occurs as well in the cell when filled with a sugar solution as in the vessel in which the precipitate may be formed. In de-

positing this membrane it has always been found necessary to employ considereably lower voltages than with other membranes under similar conditions. The highest potential which could be safely used in the first application of the membrane-forming process to a cell of the coarser variety was 12 volts, nor was any higher voltage deemed safe when, after a four days' test with a normal sugar solution, a reinforcement of the membrane was found necessary. In the third treatment of this cell, four weeks later, any attempt to go beyond 33 volts at once lowered the resistance which continued to fall until a return was made to the lower voltage.

This membrane was tried in cells of both types, and its behavior was, in general, unsatisfactory. Its activity, as manifested by the rate of flow under a pressure of 10mm. of water was about one-half that of the ferric hydroxide membrane, about one-third that of the cobalt ferrocyanide membrane, and two-thirds that of the Prussian Blue membrane under similar conditions. This comparison in the case of the ferric hydroxide membrane could be made only in the smaller cells; in the other cases the larger cells were employed.

The first cell tried was one of the larger variety.

The solutions were 1/10 normal manganese sulphate and potassium ferrocyanide, and the current from the battery with a potential of 12 volts was passed continuously during two hours and forty-five minutes; a maximum resistance of 345 ohms being reached at the end of two hours of the electrolytic action. After washing, the cell was set up with a normal sugar solution to deliver at a pressure of 10 mm.; the temperature being about 15°.0. The flow at first was at the rate of over 5 c.c. per hour, but this activity soon diminished, reaching the small figure of 9.1 c.c. per day in three and one-half days, with a total delivery of 65.5c.c. Here the membrane-forming process was repeated, a resistance of 1167 ohms being reached in one hour. At first the rate of delivery was slower than before, but the staying qualities of the firmer membrane were plainly manifest. Two weeks later with a total delivery of 177.5 c.c. the rate was still 9 c.c. per day; though from this time on the diminution was marked, only 3.7 c.c. being delivered in the same period ten days later; the total delivery in twenty-four days being 233.4 c.c.

The third attempt to build up a firm membrane in this cell showed no improvement over the second. The resistance was nearly the same, the activity of the membrane some-

what less than before, and the total amount delivered in thirty-seven days only 224.5 c.c. A fourth and fifth time similar efforts were made to reinforce this membrane. The activity as indicated by the rate of its measured delivery seemed somewhat diminished each time, while the resistance remained practically the same. A peculiarity of this cell was that after it had been set up for two or three days, the sugar solution showed a slightly yellowish tint and contained appreciable, and constantly increasing amounts, of very fine white suspended matter, not distinguishable from the manganese ferrocyanide. In sixteen days this turbid condition was quite marked both in the water surrounding the cell and in the solution within. The latter solution had become quite opaque. This characteristic was persistent throughout the whole history of the cell, not only in its numerous trials with sugar solutions, but also on being tested with alcohol. Here the delivery was of a very marked yellow color.

In other cells the yellowish tint was somewhat in evidence, but not the turbid character of the liquids within and without. Cell XXII. of the same kind and with the same membrane, duplicated in every respect, except the last the results just recorded. Two tests with cells of the

finer grade showed nothing more than that the membrane was better supported in these cells and that it continued longer in them without deterioration. The curve representing the rate of delivery as plotted against concentration showed no appreciable deterioration of the membrane during thirty-two days; and when, thirty days later, the cell was broken for the inspection of the membrane the latter was quite equal in appearance to the sound and firm ferric hydroxide membrane. With this single exception, all the ferrocyanide membranes tested showed some deterioration. This was best observed when the cell, after having been subjected to the desired number of tests, was broken, and the membrane compared in appearance with a newly formed membrane of the same type. It was also perceived by a falling off in the delivery of these cells in the later periods of their history. This deterioration consisted mainly in a partial transformation of the ferrocyanide into the corresponding oxide, though complete local removal of the membrane also took place. In the manganese ferrocyanide membrane the deterioration was chiefly of the latter kind and was very marked, being greater than in any of the other cells. In the cobalt ferrocyanide membrane both forms of deterioration took place, but in a lesser degree; while in

the Prussian Blue membrane only local removal seems to have occurred, and this to no great extent in the very thick membranes.

THE COBALT FERROCYANIDE MEMBRANE - The next membrane studied was that precipitated from cobalt sulphate and potassium ferrocyanide. This precipitate is flocculent, and quite cohesive. When freshly precipitated, it is greenish in tint, changing to a bluish green, and in very old membranes, to a purple color. There has never been any difficulty in forming a membrane from this precipitate. With 1/10 normal solutions of these salts and a battery current of 12.4 volts, the resistance of the membrane in one of the larger cells rose steadily, reaching 910 ohms at the end of two hours and thirty minutes. When set up with a normal sugar solution - the temperature being that of the laboratory and averaging between 15 and 16 - the membrane showed an activity notably greater than any hitherto observed. Without having been reinforced, this membrane continued to manifest the same high degree of activity throughout the entire period of its first test. At the end of 55 days the delivery amounted to 4c.c. per day, the total delivery had been 574c.c., and the concentration of the sugar solution

within had dropped to 1/61 normal. With no further treatment than washing with distilled water, this cell was refilled with a fresh normal sugar solution and placed in a constant temperature bath at 35 . The fact that in seven days it delivered 256.7 c.c. as compared with 226.2 c.c. for the corresponding period of the first test shows that its activity had not been seriously impaired. It also confirms observations made earlier in the history of this cell viz.: that the activity is notably greater at higher temperatures. This work was done in early January, and although the laboratory temperature approached twenty degrees in the afternoon, a somewhat lower temperature was the rule during the night and the morning hours, and the rate of delivery as indicated by the readings, and yet more strikingly by the time elapsing between the falling of successive drops from the delivery tube, followed these temperature variations quite closely. The following figures, copied from the notes taken at the time, will perhaps be of interest. They cover the 4th, 5th, and 6th days of this test.

Time.	Amt. delivered.	Temperature.	No.of Seconds.
8.50 A.M.	148.4 c.c.	----	228
10.30 "	150.5 "	$14^{o}.0$	209
12.30 P.M.	153.6 "	$17^{o}.3$	197
4.45 "	159.7 "	$19^{o}.7$	185.5
10.00 A.M.	176.8 "	$13^{o}.0$	271.5
2.00 P.M.	181.5 "	$16^{o}.3$	257
4.00 "	184.0 "	$19^{o}.7$	220
10.45 A.M.	201.0 "	$15^{o}.0$	294
12.15 P.M.	202.0 "	$16^{o}.5$	275
2.45 "	204.8 "	$18^{o}.2$	265

Similar readings were taken covering a period of ten days, and indicating the same dependence of rate upon temperature. Observations taken at the same time on the action of other cells show a repetition of these figures.

This membrane was not, however, possessed of indefinite endurance; and, after ten days of the second trial, gave evident signs of weakening. It was accordingly reinforced. A battery current of 61.5 volts was employed during a period of two hours, at the end of which time the steadily growing resistance registered 2010 ohms. A second reinforcement two weeks later developed a maximum resistance of 2040 ohms, the current employed being taken from the dynamo circuit at 103 volts. In both instances the cell fully equalled its former record for activity.

In a second cell of the same type this membrane de-

veloped a resistance of 1150 ohms in one hour and thirty minutes, the battery current being taken at 38 volts. When set up in a constant temperature bath at 35 degrees the delivery was very rapid, 9.9 c.c. in one hour, 109.6 c.c. in one day, and 275.4 c.c. in seven days. One hour's reinforcement with the battery current at 62 volts developed a resistance of 2033 ohms. The figures for delivery under the same conditions as before were: 10.0 c.c. in the first hour, 111.2 c.c. in twenty-four hours, and 296.7 c.c. in one week. When set up with a 1.3 normal sugar solution, the delivery was in two hours, 18.9 c.c., in 12 hours, 87.7 c.c., and in seven days, 387.8 c.c.

The interest attaching to the third cell in which this membrane was deposited centres mainly in the fact that this cell, despite persistent efforts, had previously failed to show any osmotic activity when tried with the ferric hydroxide membrane. In this test, after having entirely removed the previous deposits, the cobalt ferrocyanide membrane proved as satisfactory as in the two previous instances. A resistance of 1100 ohms was reached in one hour and thirty minutes, and the membrane showed satisfactory activity when tried with solutions of both sugar and alcohol - the velocity of delivery with a 90.5% solution of alcohol

amounting to 29 drops per minute, 15.5c.c. in one hour, 130 c.c. in twenty-four hours. This proves that the failures of three cells of this type to produce a satisfactory ferric hydroxide membrane, cannot be explained by a chance selection of three cups so defective that they could not manifest activity with any membrane. It shows, too, that the firmness and consistency of some membranes may enable them to exhibit good results in walls which, with other precipitates, fail completely. We also saw earlier that the ferric hydroxide precipitate, which requires a quite perfect wall, showed remarkable activity in a cup which, with ferric phosphate had given no hope of success.

This membrane was later reinforced and set up with a thrice normal sodium chloride solution, but the delivery was quite low; only 18 c.c. in twenty-four hours. The membrane seemed at the end of this time to be nearly destroyed, and the outside water, which then contained scarce more than a trace of sodium chloride, was in another twenty-four hours intensely salt. When, after prolonged washing, the reinforcement of the membrane was again attempted the resistance was no higher than when beginning a new cell in which no membrane had ever been deposited.

A fourth cell, of the same type but harder burned,

showed higher resistance - 1500 ohms in the first treatment and 3050 and 3060 ohms respectively in the first and second reinforcements. The rapidity of flow from this cell was about 20% lower than that recorded in the case of the other cells with the same membrane, but the amounts of sugar or alcohol passing through the walls of the cell were likewise much smaller. On this subject more will be said in the general discussion later on.

THE PRUSSIAN BLUE MEMBRANE - This was the last membrane taken up for study in the present investigation. It was known to be an active membrane, and its possibilities had been somewhat investigated, not thoroughly, however, and especially not in the light of the electrolytic methods of Morse and Horn. This subject is a well known, beautiful blue precipitate. Its ready cohesion and rather firm texture highly recommend it; though it is of course to be expexted that it will be liable, in much the same way as other ferrocyanides, to the destructive chemical action of some of the substances whose osmotic properties it may be desirable to determine. Here again a low voltage was found necessary, particularly at starting. In a cell of the coarser grade the attempts to secure a satisfactory mem-

brane show a record which, it is thought, will prove not uninteresting. The voltage was varied between 4.5 and 10 volts with a 1/8 normal solution of ferric sulphate surrounding the cell and a 1/10 normal solution of potassium ferrocyanide within. After two hours and fifteen minutes, a resistance of 80 ohms was indicated, which remained constant during an hour of further electrolytic action. Examination of the cell showed that all the precipitate had been formed within the walls. The cell when set up with a normal sugar solution showed no activity, and the following day the attempt to secure a membrane was repeated, the concentration of the outer ferric solution being made twice as great as on the former occasion. After a current of 12 volts had been passed through the cell during one hour and forty-five minutes, the resistance measured only 36 ohms. The precipitate had still made no appearance on either surface of the wall, and the feeble activity of the membrane ceased after having delivered 2 c.c. in twenty-four hours. The difference in concentration of the electrolytes was still further exaggerated so that now the outer iron solution was one-half normal and the potassium ferrocyanide solution one-twentieth normal. A resistance of 250 ohms was reached by four and one-half hours' electrolysis. The mem-

brane now appeared on the inner wall, and when set up, its activity was very satisfactory indeed, a rate of about 6 c.c. per hour being delivered at the beginning. This, however, after twenty hours was reduced 0.4 c.c. per hour, the delivery being of a marked blue tint. On the fourth attempt the deposition of the membrane was continued two hours and forty-five minutes. The resistance was 255 ohms and the membrane though less active was more permanent than before, delivering 111 c.c. in thirteen and a half days.

A fifth time the membrane-forming process was repeated, using the same potential, 12 volts, and a resistance of 285 ohms was measured at the end of two hours' treatment. The activity and permanence of the membrane were much as before, but no blue color appeared. The sixth and seventh efforts represented about one hour each of electrolysis, at potentials of 62 and 105 volts, and resistances of 1080 and 1097 ohms respectively were recorded. In both cases the membrane was quite satisfactory, both in point of permanence and of activity. In the broken cell, the two membranes formed within the wall are plainly to be seen and the membrane on the inner edge of the wall is of great thickness.

With the second cell, again of the coarser type, sat-

isfactory results were more quickly obtained. A large amount of ferric hydroxide precipitate had been deposited within the walls of this cell in previous fruitless efforts to form an active membrane of that material, and without removing this, the formation of the new membrane was begun. In order to secure the thickness which seemed necessary in this membrane, a strong current was employed, as much as 0.7 amperes being passed through the cell; but the results were all unsatisfactory until the relative concentration of the electrolytes was made widely different. The concentration of the inner electrolyte was kept 1/10 normal throughout; the outer solution of ferric sulphate being changed from 1/5 to 1/2 normal. Under these conditions the resistance rose satisfactorily, reaching 371 ohms in the first treatment, 1200 ohms in the second, and 2240 ohms in the third, when, finally, a very satisfactory membrane was obtained. Subsequent examination disclosed the fact that this membrane was extremely thick, local maxima reaching dimensions of 0.4 mm.

With the smaller cells resistances of 17000 and 54000 ohms were obtained. These membranes were active with solutions of sugar, alcohol and sulphuric acid; but in the case of the latter the leakage was large and the delivery

soon ceased.

GENERAL CONCLUSIONS.

The final test of all these membranes must be made in cells whose walls are capable of giving sufficient support to the membrane throughout its entire area. Until such a cell is obtained, we must conclude that the manganese ferrocyanide membrane is unpromising both in point of permanence and activity; that the ferric phosphate membrane is purely problematical; that the ferric ferrocyanide membrane is satisfactorily active, and is the most permanent of the ferrocyanide membranes here tried; that the cobalt ferrocyanide has sufficient permanence for purposes of measurement, and possesses moreover very great activity, together with a firmness and consistency far superior to those of other membranes experimented with; finally, that the ferric hydroxide membrane offers both permanence and great activity, but is incapable of manifesting the latter property except in cells whose walls are of a quite uniformly fine texture.

We may now turn our attention to the consideration

of such questions as whether these membranes are completely or only partially semipermeable, i.e., do they altogether prevent or merely retard the passage of dissolved substances; whether the flow of water through the membrane is proportional to the difference in concentration of the solutions separated by the membrane; whether the diminution of concentration within the cell bears any fixed ratio to the volume which it has delivered and whether the deficiences observed are due to defective cell walls; and, if so, can they be remedied.

In answering the first question it must be said that in every one of the many cases observed there has been leakage through the walls of the cell. Hence, either the membrane or the wall is defective; perhaps both. The evidence all points towards the deficiency of the wall. This evidence is, first, the fact that in all cases in which the deposition of the membrane was long continued a maximum resistance was reached, which ordinarily became constant for all further treatment. This fact seems capable of explanation only on the supposition that there is a constant cross-section of unimpeded transferrnce of the ions; or, in other words, a number of pores too large to be bridged over by the membrane.

Second. The much larger leakage when the cell is delivering under somewhat greater pressures. Three examples taken from a number of these observed differences will suffice. Cell XVII. set up with a solution containing 60.0 grms. of sugar to deliver at a pressure of 10 mm. water. Leakage of sugar in 10 days, 21 1/2 hours, 4.532 grms. The same cell immediately set up with 60.0 grms. sugar to deliver at 174 mm. pressure. Leakage in 10 days, 20 hours, is 6.587 grms. Cell XXII set up with normal sugar, to deliver at 10 mm. Leakage, 5.074 grms. in 7 days, 50 minutes. The same cell and same concentration to deliver at 74 mm. Leakage in 7 days, 70 minutes, 7.052 grms. Cell XV., 60 grms. sugar. Leakage during 10 days, 22 hours at 10 mm. pressure, 4.354 grms. At 222 mm. pressure in 10 days, 19 hours, leakage 7.077 grms. Now, if the membrane is intact this leakage is simply the measure of the diffusion of the dissolved substance; and the rate of diffusion of a given substance through a given medium, the temperature remaining unchanged, depends only upon its concentration. This is not appreciably changed by these slight pressures. Consequently, not diffusion merely, but a positive outward flow of the solution takes place; hence there are interstices which make this movement possible.

Third. The same membrane, cobalt ferrocyanide, prepared with equal care, gives in different cells widely different amounts of leakage. The thickness of the semipermeable membrane should, if the area is the same, vary with the number of Coulombs represented by its formation. Hence, in cell XXI., in the formation of whose membrane 0.19 ampere hours were used, the membrane should be not appreciably thicker than in cell XIX., whose membrane represents 0.17 ampere hours of current. And if the leakage is to be explained by diffusion there should be no wide difference here. Yet, the leakage through cell XXI., viz., 0.8904 grms. sugar in 7 days, 23 hours, was much less than through the other wall. The number for this is 5.458 grms. sugar in 12 days, 2, 1/2 hours. Again, for cell XXI. set up with a solution containing 74.33 grms. alcohol we have the small leakage of 0.2077 grms. in 11 days, 23 hours; while in cell XX. with the same membrane and set up with 127.2 grms. of alcohol we have a leakage of 3.540 grms. in 10 days, 18 hours. The same cell, XXI. - with the advantage, however, of a reinforcement of the membrane - shows a smaller leakage with the much smaller and more active alcohol molecule than that recorded for the sugar; while, if diffusion were the explanation, the opposite result should have been

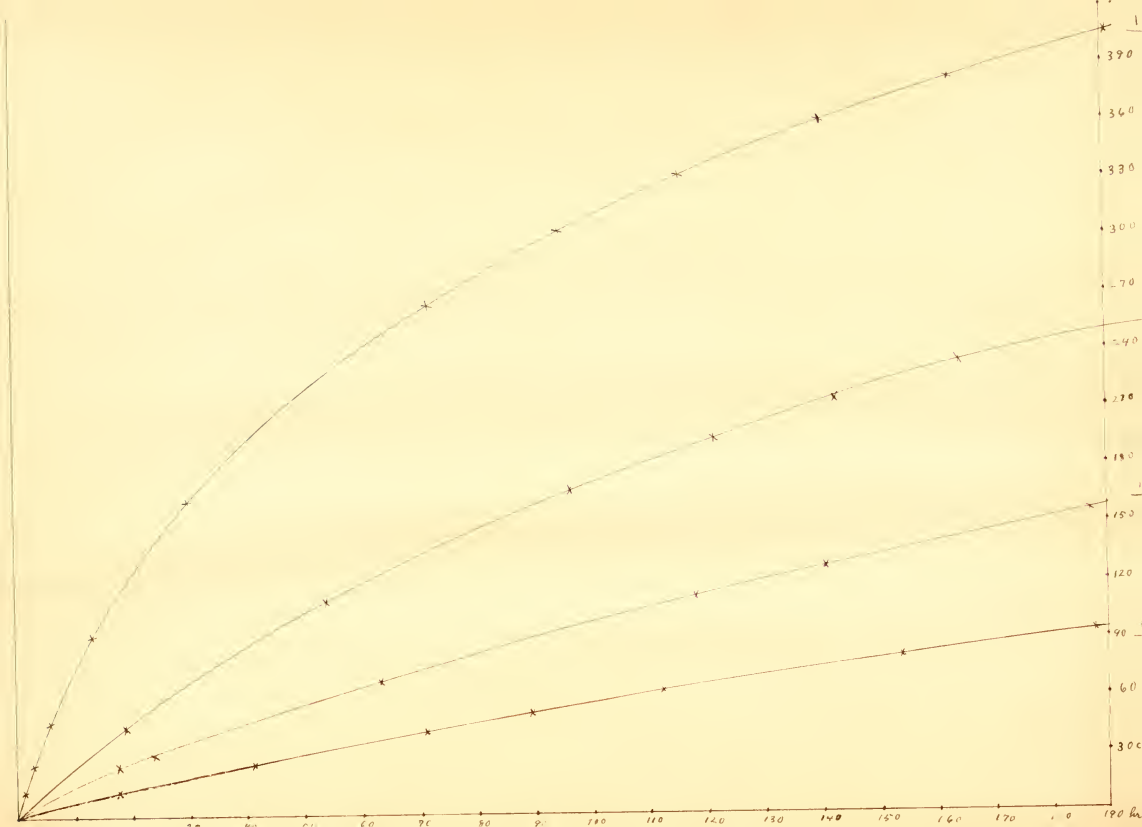
observed. The figures for cell XXI., both in point of delivery and smallness of leakage, show that this membrane is semipermeable quite as well for the smaller alcohol molecule as for the larger molecule of sugar. The evidence, such as it is, favors the complete semipermeability of the membrane, though a demonstration is hardly possible with the means at hand.

The answer to the question: Is the flow through the membrane, of the pure solvent from without, proportional to the concentration of the solution within? seems to be the same both in theory and practice. The rate of flow increases with higher concentrations, but not in a direct ratio. This is to be expected if we consider that the porous wall offers a very high resistance to the rapid passage of a liquid. Hence, the greater the concentration and the more rapid the flow, the more effectively will this resistance be felt. Again, the rapid influx of water through the membrane dilutes more appreciably the solution immediately adjacent to the membrane, thus reducing the effective concentration of the solution, and, in consequence, the flow through the membrane. Further, there is a dependence upon the relative densities of the solutions employed. In the sugar solution the density exceeds that of the outer water,

and the dilution of the portions adjacent to the membrane makes this part lighter than the remaining liquid, giving, in consequence, upward currents along the cell wall toward the point of delivery. The solution delivered is, therefore, of lower density than the average concentration remaining within the cell. While if alcohol be used, the opposite results must take place, the more concentrated solution being first delivered, and the greater density of the lower concentration adjacent to the membrane causing this to flow downward. All these will have their influence in producing a rate of delivery somewhat different from that which should result from a uniform concentration of the solution within the cell. If now we turn from theory to the figures observed, we find the flow from cell XVI. at a concentration 1/45 normal to amount to 7.7 c.c. per day. The proportional flow for a normal solution would be more than 346 c.c. per day under the same conditions of temperature. These temperature conditions were identical when seven days later with a fresh solution of normal sugar this same cell exhibited an initial flow of 293c.c. per day - a difference quite appreciable, yet, perhaps, not so great as we should expect with these large figures. The measurements from which comparisons are drawn, must, unless

corrections can be applied, be taken when the outer solvent is pure. For instance, in cell XVI. at a concentration 1/45 normal the flow was twice as great as when this concentration was 1/61 normal, because of the presence of a very small amount of sugar in the outer water at the latter concentration. This same cell at a concentration of 0.03 grms. per c.c., when the amount of sugar in the outer water had risen to 0.020 grms. per c.c. trebled its flow on replacing the latter by pure distilled water. The difference of the concentrations within and without had been 0.01 grms. per c.c. in the former instance, and was three times that after the change. This showed that at low concentrations the flow is very nearly in direct proportion to the difference of concentration of the inner and outer liquids; also that unless the outer water is pure or its concentration known, the flow from a given cell cannot be taken as a measure of the activity of its membrane at the actual concentration of the solution within; the more so if this concentration be rather low, for then the concentration of the outer liquid may easily represent a large percentage of the concentration within, and the flow through the membrane will be diminished in the same ratio. As the leakage from the cells was in most cases allowed to accumulate and no

accurate knowledge of its concentration was attempted until several days had passed, the many readings taken represent accurately the relative activities of the various membranes at the beginning only of the record and at the end when it was corrected for the outer concentration, then measured. Still, all the earlier readings taken while the concentration of the outer liquid was an inappreciable fraction of the high concentration within, are close approximations to the correct values. Hence, the curves of several of the typical cells are here given. The total delivery is plotted against time and the slope of the curve represents the rate of flow of the cell for the corresponding time.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Curve I. illustrates the action of a cobalt ferrocyanide membrane in Cell XIX. when set up in a constant temperature bath at 35°. The sugar solution was 1.3 normal.

Curve II. represents the activity of the same membrane in Cell XVI. when set up with a normal sugar solution at the temperature of the laboratory - about 18°.

Curves III. and IV. are for the Prussian Blue and Manganese ferrocyanide membranes. The conditions are the same as those last given. These three are good types of the records made by the respective membranes.

The relation between the total volume delivered and the diminishing concentration within the cell is also interesting. If we suppose diffusion to prevent differences of concentration in the different portions of the cell, this relation is easily worked out as follows: Let V = the capacity of the cell and v the total volume delivered. Then v is the independent variable and the concentration, K, is a function of v and may be written $K = \varphi(v)$. The total dissolved substance in the cell at any time is, then, $V\,\varphi(v)$, the amount at starting being equal to $V\,\varphi(0)$. Now when v receives the increment dv, the substance lost by the cell is $\varphi(v)\,dv$.

This quantity can also be expressed by representing the difference between the total amounts of dissolved material in the cell before and after the delivery of the volume dv. Hence we have

$$\varphi(v)dv = V\varphi(v) - V(\varphi(v) + d\varphi(v)) = -Vd\varphi(v).$$

Hence $$\frac{d\varphi(v)}{\varphi(v)} = -\frac{dv}{V};$$

Whence $$\log_\epsilon \varphi(v) = -\frac{v}{V} + C.$$

Now making $v = 0$, we have $\log_\epsilon \varphi(0) = C$.

and subtracting, $$\log_\epsilon \varphi(v) - \log_\epsilon \varphi(0) = -\frac{v}{V} = \log_\epsilon \frac{\varphi(v)}{\varphi(0)}.$$

But the ratio $\frac{\varphi(v)}{\varphi(0)}$ expresses in terms of the original concentration of the cell, the concentration remaining after the volume v has been delivered. Hence we may write

$$\log_\epsilon K = -\frac{v}{V}, \text{ or}$$

$$K = e^{-\frac{v}{V}} = \left(\frac{1}{e}\right)^{\frac{v}{V}}$$

Hence the concentration of the cell, taking the original concentration as unity, is represented by the above fraction - in which e is the base of the Naperian system of logarithms - raised to the power which is expressed by the ratio between the amount delivered and the capac-

ity of the cell. When the value of this exponent becomes 1, 2, 3, 4, etc., the values of K are 0.36788, 0.13533, 0.049788, 0.018315, etc. We have seen that in practice we may expect these values to be exceeded when the density of the solution is greater than that of the solvent, and, when the density of the solvent is the greater, to be not attained.

Leakage is another factor which must be taken into consideration. Its effect is, in all cases, to diminish the concentration; and this must be borne in mind whenever comparisons are made between the results above deduced and the figures actually observed in the laboratory. If the test of the cell covers a long period of time, as in the 55 days trial of cell XVI. this factor of leakage is very important. The rate of flow becomes quite small, and the amount of solution passing through the walls may reach a magnitude almost equal to the delivery. In this case the final concentration, instead of being greater than the figures above given, will be much less. The figures observed for this cell, No. XVI., are: computed residual concentration after a delivery of 574 c.c., 0.01541 grms. per c.c.; actual, 0.00554 grms. per c.c. If now we take cell XXI. in which the leakages of both sugar and alcohol were small, we

find the concentrations in the case of the sugar solution to be: deduced, 0.3889 normal; actual, 0.4261 normal. Here the time was 7 days, 23 hours, and the leakage, 0.8904 grms. And for alcohol - the time being 11 days, 23 hours, and the leakage, 0.2077 grms. - deduced, 0.1308 normal; actual, 0.09698 normal. These examples show clearly that the upward currents of the sugar solution when diluted at the cell wall by the entering water, and the downward currents of the diluted alcohol solution, take place as was previously surmised, and that a liquid of less density than the average concentration of the inner solution, is constantly being delivered. This is clear also from the recorded measurements of the concentrations of small amounts just delivered, and of the residual liquids in the cells. In cell XXII., set up with sugar, the 41.3 c.c. just delivered, had a concentration of 0.1911 grms. per c.c., while the average concentration of the inner liquid after delivering the above was 0.2062 grms. per c.c. And for cell XX., set up with alcohol, the density of the solution just delivered was 0.9824, as contrasted with a density 0.9891 for the liquid within.

THE CELL WALL.

We may add to the evidence on this question thus far considered, the fact that out of a lot of 100 cells which gave the best results in all work done in this laboratory, a very small number - the least porous among them - gave really good results. Work done by several investigators in the earlier part of the present year led to the conclusion that the unsatisfactory work was due to deficiencies in the wall. It was hoped that some method might be discovered of remedying these defects. The first attempt was made with kaolin in an extremely fine state of division and suspended in a liquid which was forced through the walls both by electrolytical methods and by pressure. This deposit was by no means firm enough to give the desired support. After a repetition of this process, the deposits of kaolin were cemented, as far as this could be accomplished, by a superimposed electrolytic deposit of barium sulphate. This attempt to remedy the cell was likewise without satisfactory result. The purpose of the next step was, by means of a strong current, to completely fill the porous wall with the barium sulphate precipitate. But no high electrical resistance could be obtained, and hence it seemed im-

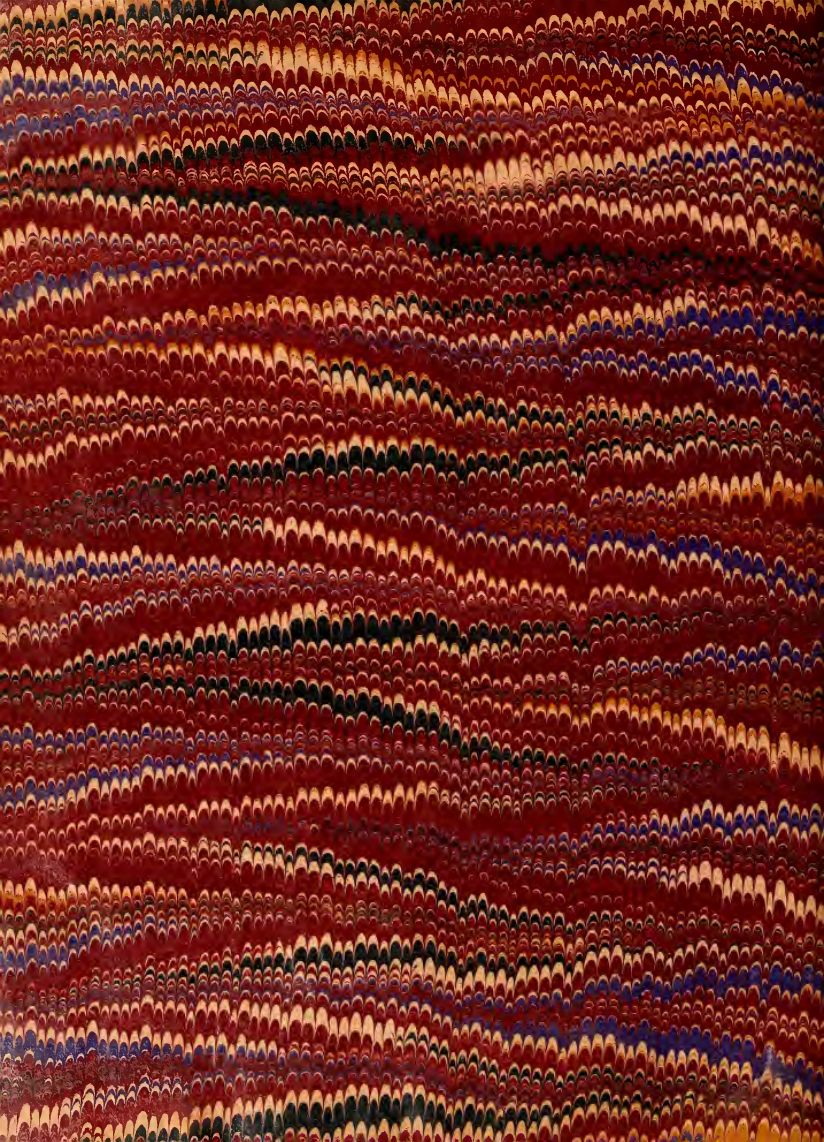
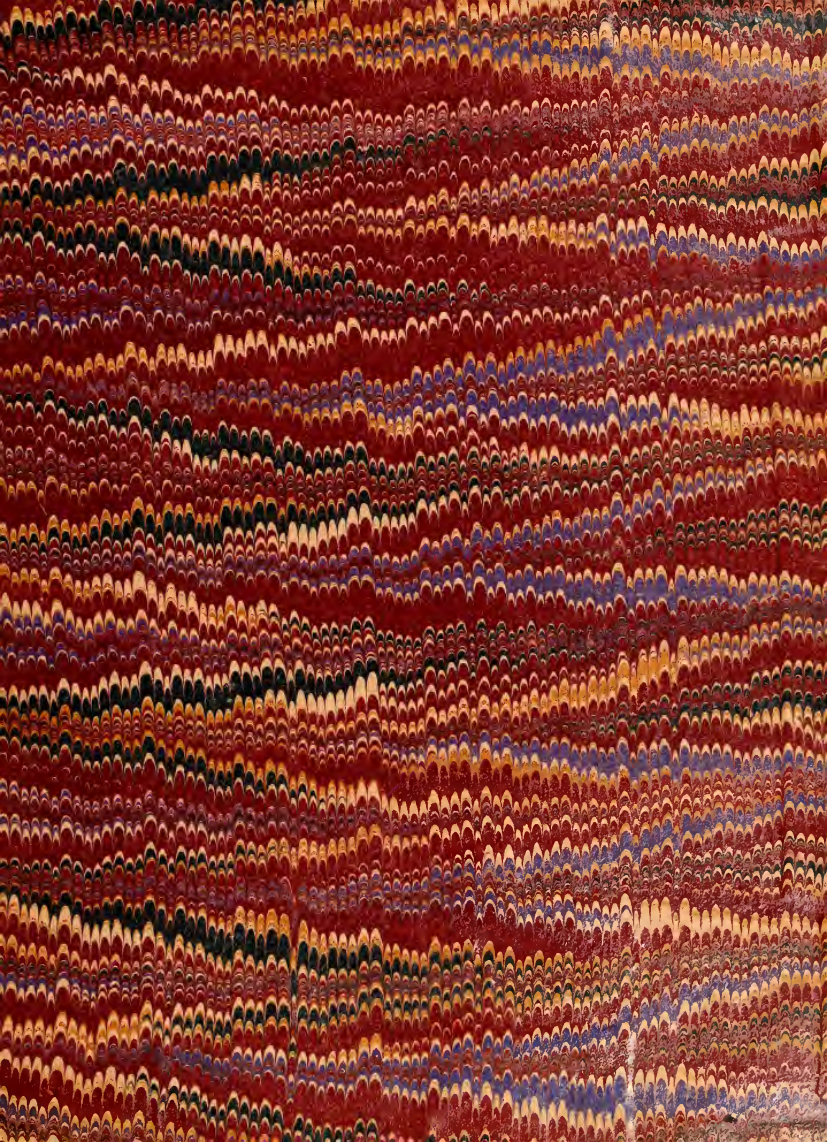
p ssible to entirely fill the cell with this material. Efforts to form a membrane after these treatments were not more successful than those which had preceded. The membrane seemed to form in portions of the cell not occupied by the other materials. The appearance of the cell was most unsatisfactory; the membrane appeared in great blotches on the inner and outer edges of the wall, and, on breaking the latter, it was found in all possible positions within the wall. Efforts were also made to block these pores with some one of the various membranes tried, but this had the same result as that reached in all preceding attempts. None of the methods employed by the different investigators seemed to produce any appreciable improvement.

ADDENDUM.

Those whose interest has carried them thus far will be gratified to learn that at this stage of the work Morse and Frazer carried out in this laboratory a thorough microscopic investigation of the cells tried the previous year and found to give either good, bad or indifferent results.

In all these cases the character of the cell wall was found closely related to the reliability of the cell for the measurement of high pressures. In the good cells there were no large pores present, and the greater or smaller number of these in the other cells could be inferred before examination on a mere inspection of the record of the cell.

After an exhaustive study of the probable causes of the existence of these pores, and their possible remedies, the above named workers, after assuring themselves that the American potters would not attempt this problem, set themselves the task of producing the desired perfect wall. The extreme care shown in all details, the method and thoroughness of the work thus far carried out promise early and complete success. The production of such a wall will, it is confidently hoped, mark the beginning of real quantitative work in the field of osmotic phenomena. And this, in turn, will lead to the unravelling of some very important and intricate problems, the solution of which, depends upon this accurate knowledge of osmotic activity.

BIOGRAPHICAL.

The writer was born in Edina, Missouri, July 22, 1862. His early education was received in the parochial schools of his native town, and from private tutors. In 1884 he entered St. Mary's College, Kansas, and in 1886-7 he taught in the Grammar Department of St. Francis' Institute, Osage Mission, Kansas. With the exception of two years spent in Theological and Biblical studies at Woodstock College, Maryland, the next fourteen years were spent by him in following the Ascetical, Classical, Scientific, Metaphysical, Ethical, Exegetical and Theological courses offered in the Normal and Graduate schools of the St. Louis University, St. Louis, Missouri. During four years of this period, he also occupied the position of Assistant in Mathematics. Since October 1, 1901, he has pursued graduate studies in Chemistry at the Johns Hopkins University. His subordinate subjects are Physical Chemistry and Geology.